Title	Studies on the electrochemical properties of copolymers of maleic acid, II : potentiometric titration at high ionic strength
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Citation	The Review of Physical Chemistry of Japan (1960), 30(2): 145-154
Issue Date	1960-12-30
URL	http://hdl.handle.net/2433/46796
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Type	Departmental Bulletin Paper
Textversion	publisher

THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 30, NO. 2, DEC. 1960

STUDIES ON THE ELECTROCHEMICAL PROPERTIES OF COPOLYMERS OF MALEIC ACID, II

Potentiometric Titration at High Ionic Strength

BY KAZUO MONOBE

(*Received October 31*, 1960)

The potentiometric titrations of two copolymers, maleic acid-vinyl acetate and maleic acid-styrene copolymers, were carried out at high ionic strength. The dissociation constants, pK_1° and pK_2°, in which the influence of polyion potential was fully eliminated, were evaluated by means of the titration results and compared with the corresponding values of proper α, β-disubstituted succinic acids. The results were examined in detail, assuming that the nearest neighbor interaction was independent of the ionic strength. As a result, the $\Delta pK'$ value which represents the difference between pK_2° and pK_1° in the vinyl acetate copolymer, was regarded as a rather reasonable value, judging from the localized electrostatic neighbor interaction. On the other hand, the larger $\Delta pK'$ value in the styrene copolymer was attributed to the fact that the neighbor interaction was fairly apart from the localized type.

Introduction

In the previous paper[1], it was shown that the titration curves of maleic acid–vinyl acetate (MA–VAc) copolymer and maleic acid–styrene (MA-S) copolymer at low ionic strength could be represented empirically by the equations;

$$\mathrm{pH} = pK_1 + n_1 \log \frac{\alpha'}{1-\alpha'} \qquad (1)$$

and

$$\mathrm{pH} = pK_2 + n_2 \log \frac{\alpha'-1}{2-\alpha'}, \qquad (2)$$

where the pK_1 and pK_2 are the average dissociation constants for the primary and secondary carboxyl groups, respectively. The n_1 and n_2 are the empirical constants and α' represents the degree of ionization.

Equations (1) and (2) can be an empirical description for the titration curves at high ionic strength, so far as the relation, $pK_1 \ll pK_2$, preserves. In general, by the addition of neutral salts such as NaCl, the polyelectrolytes diminish the strong electrostatic force which comes from the charged groups on a polymer chain[2]. Thus, the dissociation constants, pK_1° and pK_2°, may be obtained from the titration curves in the presence of the highly concentrated NaCl independent

1) K. Monobe, *This Journal*, **30**, 138 (1960)
2) See, for example, A. Katchalsky, J. Mazur and P. Spitnik, *J. Polym. Sci.*, **23**, 513 (1957)

of the polyion field effect. Assuming that the nearest neighbor interactions are independent of the ionic strength, the interactions may be estimated from the difference between pK_2° and pK_1°.

In the present paper, the author will estimate the nearest neighbor interaction[3] of polydicarboxylic acid by means of the titration data at high ionic strength, and compare it with the corresponding monomeric dibasic acids.

Experimentals

Two copolymers of maleic acid which were copolymerized with vinyl acetate and with styrene were titrated with 0.5 N NaOH in various concentrations of NaCl aqueous solutions.

The reproducibility of the titration data was 0.02 pH unit. During titration, solutions were kept at 20.0±0.1°C and in nitrogen atmosphere to protect from CO_2. The details were given in the previous paper[1].

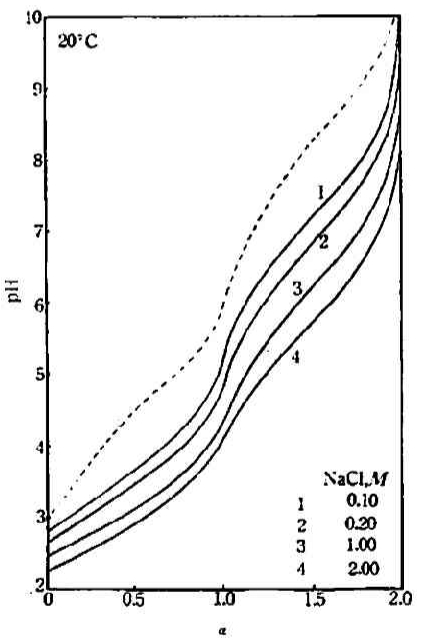


Fig. 1 Titration curves for MA-VAc copolymer (20°C)

Polymer concentration, 0.986×10^{-2} M; NaCl concentrations, 0.10 M (1), 0.20 M (2), 1.00 M (3), 2.00 M (4). Dashed line; in the absence of NaCl.

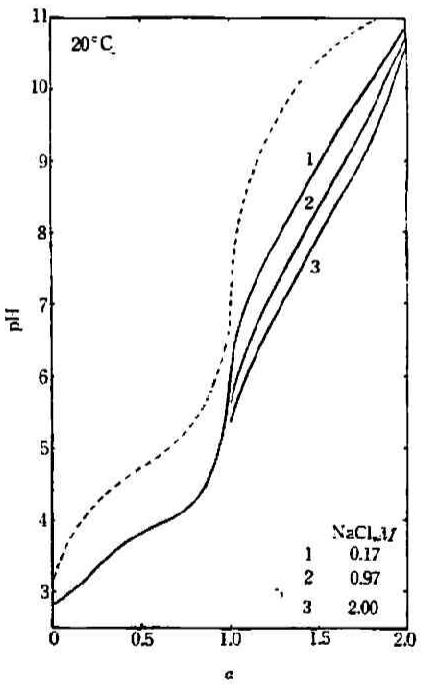


Fig. 2 Titration curves for MA-S copolymer (20°C)

Polymer concentrations ($M\times10^2$) and NaCl concentrations (M); 0.79·0.17 (1), 0.93, 0.97 (2), 0.96, 2.00 (3), 0.96, 0 (dashed line).

3) Reference 2), Discussion

Results

Titration curves of MA–VAc copolymer and MA-S copolymer in various concentrations of NaCl aqueous solutions are shown in Figs. 1 and 2.

As is shown in the figures, the pH values of solutions at the same degree of neutralization decrease with increasing NaCl concentration. In Fig. 1 for MA–VAc copolymer, the marked transition between the primary and secondary dissociation processes still remains even in the presence of NaCl of high concentration.

In Fig. 2 for MA-S copolymer, the latter half of the titration curves were plotted only, at high ionic strength, because of the precipitation tendency during the dissociation of primary carboxyl group. This means the marked difference in the salting-out effect between the region of $\alpha<1$

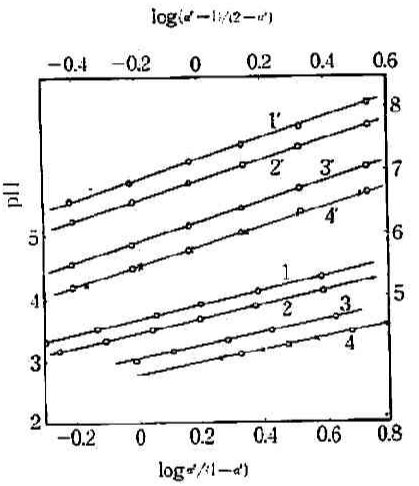


Fig. 3 Plots of pH against $\log\frac{\alpha'}{1-\alpha'}$ or $\log\frac{\alpha'-1}{2-\alpha'}$ for MA-VAc copolymer

The scales for primary dissociation processes, 1, 2, 3 and 4, are the lower and left, and for secondary dissociation processes, 1′, 2′, 3′ and 4′, are the upper and right.

	Polymer conc.	NaCl conc.
1, 1′	$0.986\times^{-2}M$	$0.10M$
2, 2′	$0.936\times10^{-2}M$	$0.20M$
3, 3′	$0.986\times10^{-2}M$	$1.00M$
4, 4′ (○)	$0.986\times10^{-2}M$	$2.00M$
4, 4′ (×)	$1.062\times10^{-2}M$	$2.00M$

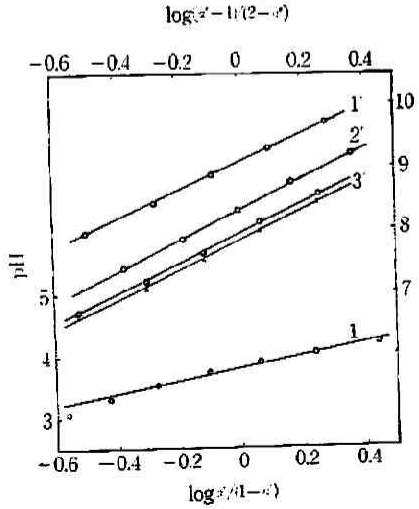


Fig. 4 Plots of pH against $\log\frac{\alpha'}{1-\alpha'}$ or $\log\frac{\alpha'-1}{2-\alpha'}$ for MA-S copolymer

The scales for primary dissociation process, 1, are the lower and left, and for secondary dissociation processes, 1′, 2′ and 3′ are the upper and right.

	Polymer conc.	NaCl conc.
1, 1′	$0.794\times10^{-2}M$	$0.17M$
2′	$0.931\times10^{-2}M$	$0.97M$
3′ (○)	$0.963\times10^{-2}M$	$2.00M$
3′ (×)	$0.120\times10^{-2}M$	$2.00M$

The Review of Physical Chemistry of Japan Vol. 30 No. 2 (1960)

and of $1<\alpha$, where α represents the degree of neutralization.

The application of Equations (1) and (2) to these results gives Figs. 3 and 4, and Tables 1 and 2.

Table 1 Dissociation constants for MA–VAc copolymer (20°C)

NaCl, M	Copolymer, $M\times10^2$	pK_1	n_1	pK_2	n_2
0	0.986	4.50	1.40	8.25	1.46
0.10	0.986	3.65	1.15	7.20	1.62
0.20	0.986	3.44	1.08	6.85	1.60
1.00	0.986	3.03	1.00	6.20	1.60
2.00	0.986	2.77	1.00	5.80	1.56
2.00	1.062	2.77	1.00	5.80	1.56
2.00	0.354*	—	—	5.78	1.56
2.00	0.133*	—	—	5.75	1.56

* The pK_1 and n_1 values could not be obtained because the primary dissociation approached to the complete dissociation.

Table 2 Dissociation constants for MA–S copolymer (20°C)

NaCl, M	Copolymer, $M\times10^2$	pK_1*	n_1*	pK_2	n_2
0	0.961	4.55	1.0	10.37	2.00
0.20	0.794	3.80	1.0	9.08	2.24
0.97	0.931	—	—	8.32	2.30
2.00	0.963	—	—	7.95	2.30
2.00	0.321	—	—	7.95	2.30
2.00	0.120	—	—	7.85	2.30

* At high ionic strength, the pK_1 and n_1 values could not be obtained because of precipitation.

Evaluation of pK_1° and pK_2°

1 pK_1° During the primary dissociation process, the dissociation of the secondary carboxyl group may be neglected, as long as the polymer concentrations are not low. Therefore, the primary dissociation process may be regarded as same as that of other polymonocarboxylic acids; that is, when more than 1 M of NaCl present in 0.01 M MA–VAc copolymer solution, the contribution of the electrostatic potential of polyion may be fully eliminated. Thus, if the term depending on the ionic strength is taken into consideration, Equation (1) may be rewritten as

$$pK_1 = \mathrm{pH} - \log\frac{\alpha'}{1-\alpha'} = pK_1^\circ - \frac{0.43\,\varepsilon^2\kappa}{3\,DkT}, \qquad (3)$$

where

ε, electronic charge

κ, Debye-Hückel parameter

D, dielectric constant of solvent

k, Boltzmann constant

T, absolute temperature.

The pK_1° values for MA–VAc copolymer evaluated by Equation (3) are given in Table 3.

Table 3 The parameter pK_1° for MA–VAc copolymer (20°C)

NaCl, M	pK_1	$\frac{0.43\,\epsilon^2\kappa}{3\,DkT}$	pK_1°
1.00	3.03	0.33	3.36
2.00	2.77	0.47	3.24
			Av. 3.30±0.06

On the other hand, for MA–S copolymer, the pK_1 value at high ionic strength was not obtained, so that the contribution of the electrostatic potential of a polyion at the intermediate ionic strength must be corrected. At the intermediate ionic strength, pK_1 which is given by Equation (3) and is constant at high ionic strength, is no longer constant but a function of the potential ψ_1.

Now we denote this quantity at the intermediate or low ionic strength by pG_1.

$$pG_1 = \mathrm{pH} - \log\frac{\alpha'}{1-\alpha'} = pK_1^\circ - \frac{0.43\,\epsilon^2\kappa}{3\,DkT} + \frac{0.43\,\epsilon\psi_1}{kT}. \qquad (4)$$

The potential ψ_1 is the function of α' and is zero at $\alpha'\to 0$. Extrapolating the plot of pG_1 against α' to $\alpha'\to 0$, the pK_1° for MA–S copolymer is obtained according to Equation (4').

$$\lim_{\alpha'\to 0} pG_1(\alpha') = pK_1^\circ - \frac{0.43\,\epsilon^2\kappa}{3\,DkT}. \qquad (4')$$

We obtain $pK_1^\circ = 2.9\pm0.1$ from the extrapolated values of four curves of $pG_1 = f(\alpha')$ (see Fig. 5),

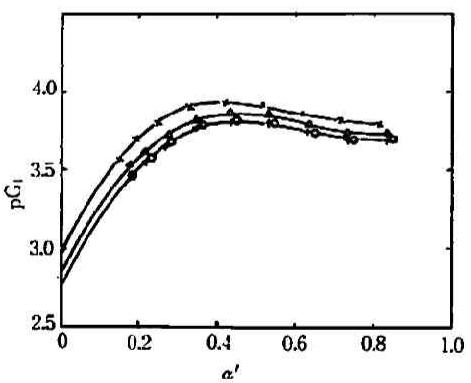


Fig. 5 Plots of pG_1 against α' for MA–S copolymer

Polymer concentrations ($M\times10^2$) and NaCl concentrations (M); (×) 0.961, 0.100, (△) 0.793, 0.170, (+) 1.059, 0.178, (○) 0.866, 0.220

where polymer concentrations and NaCl concentrations were $0.79\times10^{-2}\,M$, $0.17\,M$; $0.87\times10^{-2}\,M$, $0.22\,M$; $1.06\times10^{-2}\,M$, $0.18\,M$ and $0.96\times10^{-2}\,M$, $0.10\,M$, respectively.

2 pK_2° During the secondary dissociation, the contribution of the electrostatic potential has not been fully reduced, as shown in the results for $n_2>1$, in Tables 1 and 2. Consequently, the following extrapolation method was here tired to evaluate the pK_2° value.

A general form[4,5] of empirical Equation (2), with some transformation, may be represented by the equation:

$$pG_2 = \mathrm{pH} - \log\frac{\alpha'-1}{2-\alpha'} = pK_2^\circ - \frac{0.43\,\varepsilon^2\kappa}{3\,DkT} + \frac{0.43\varepsilon\psi_2}{kT}, \qquad (5)$$

where ψ_2 represents the electrostatic potential of a polyion at the secondary dissociation process, and is the function of α'.

As the value of pK_2 (for example, 5.80 at $2\,M$ NaCl for MA–VAc copolymer) is quite larger than that of pK_1 (2.77 at $2\,M$ NaCl for MA–VAc copolymer), the value of ψ_2 is assumed to approach to the value of ψ_1 when α' approaches to 1, where ψ_1 represents the potential of polyion due to the dissociation of the primary carboxyl group alone. The term, $\frac{0.43\,\varepsilon^2\kappa}{3\,DkT}$, is independent of α' at high ionic strength. We shall assumed that $\psi_1=0$ at the concentration of NaCl of more than $1\,M$. Hence, Equation (5) may be written as Equation (5′)

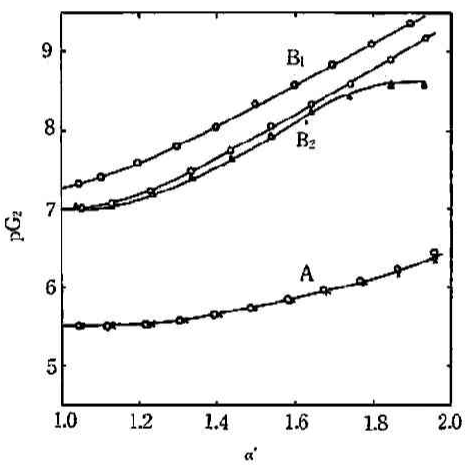


Fig. 6 Plots of pG_2 against α'

curve A; MA–VAc copolymer
Polymer concentrations ($M\times10^2$) and NaCl concentrations (M), 0.986, 2.00 (○), 0.133, 2.00 (×)

curves B_1 and B_2; MA–S copolymer
Polymer concentrations ($M\times10^2$) and NaCl concentrations (M), 0.931, 0.97 (○), 0.963, 2.00 (○), 0.120, 2.00 (△)

Table 4 The parameter pK_2° for MA–VAc and MA–S copolymers

NaCl, M	Copolymer, $M\times10^2$	$(pG_2)_{\alpha'=1}$	$\frac{0.43\,\varepsilon^2\kappa}{3\,DkT}$	pK_2°
2.00	MA–VAc, 1.062	5.50±0.03	0.47	5.97±0.03
2.00	MA–VAc, 0.986		0.47	
2.00	MA–VAc, 0.354		0.47	
2.00	MA–VAc, 0.133		0.47	
0.97	MA–S, 0.931	7.25	0.33	7.58
2.00	MA–S, 0.963	7.00	0.47	7.47
2.00	MA–S, 0.321	7.00	0.47	
2.00	MA–S, 0.120	7.00	0.47	
				Av. 7.52±0.06

4) G. S. Hartley and J. W. Roe, *Trans. Faraday Soc.*, **36**, 101 (1940)
5) H. Edelhoch and J. B. Bateman, *J. Am. Chem. Soc.*, **79**, 6093 (1957)

$$\lim_{\alpha'\to 1} pG_2(\alpha') = pK_2^\circ - \frac{0.43\,\varepsilon^2\kappa}{3\,DkT} \quad . \qquad (5')$$

The pG_2 values are shown as the function of α' in Fig. 6 and the pK_2° values according to Equation (5') are given in Table 4. Fig. 6 shows the increase of the potential with α' and the tendency is more marked in MA–S copolymer than in MA–VAc copolymer.

Comparison with Corresponding Monomeric Acids

The pK_1° and pK_2° may be regarded as the parameters corresponding to pK_1 and pK_2 for proper monomeric dibasic acid. The comparison of pK_1° and pK_2° values for the copolymers with the dissociation constants of α, β-disubstituted succinic acids, R′CH(COOH)CH(COOH)R″, are shown in Table 5.

Table 5 Dissociation constants of α, β-disubstituted succinic acids, R′CH(COOH)CH(COOH)R″ (25°C)

	R′	R″	m. p.	pK_1	pK_2	$\Delta pK'$	reference
(a)	H	H		4.19	5.48	1.29	i
(b)	C_2H_5	H		4.07	5.89	1.82	ii
(c)	CH_2–$COOCH_3$	H		4.12			ii
(d)	CH_3	CH_3	209°	3.73	5.94	2.21	i
(e)	CH_3	CH_3	129°	3.94	6.20	2.26	i
(f)	C_2H_5	C_2H_5	192°	3.63	6.46	2.83	i
(g)	C_2H_5	C_2H_5	129°	3.51	6.60	3.09	i
(h)	MA–VAc	Copolymer		3.30	5.97	2.67	
(i)	MA–S	Copolymer		2.9	7.52	4.6	
(j)	C_6H_5	H		3.79			ii
(k)	C_6H_5	C_6H_5	229°	3.70			ii
(l)	C_6H_5	C_6H_5	183°	3.58			ii
(m)	CH_2–C_6H_5	H	160°	4.04			ii
(n)	C_6H_5	CH_3	192°	3.43			ii
(o)	C_6H_5	CH_3	170°	3.63			ii
(p)	CH_2–C_6H_5	CH_3	160°	3.66			ii
(q)	CH_2–C_6H_5	CH_3	138°	3.61			ii
(r)	CH_2–C_6H_5	C_2H_5	154°	3.58			ii
(s)	CH_2–C_6H_5	C_2H_5	122°	3.38			ii

i) *Landolt-Börnstein Tab.* Erg. III ii) *Landolt-Börnstein Tab.* Hauptwerk

The very interesting results for the present purpose may be drawn out from the considerations of Table 5. In Table 5, the $\Delta pK'$ represents the difference between pK_2 and pK_1, and is related to the electrostatic interaction energy $\varepsilon^2/D_K r$ by the Bjerrum[6]-Kirkwood[7] equation:

6) N. Bjerrum, *Z. phys. Chem.*, **106**, 219 (1923)
7) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506, 513 (1938)

$$\Delta pK' = pK_2 - pK_1 = \log\sigma + 0.43\,\varepsilon^2/D_K rkT \ , \qquad (6)$$

where r, distance between the primary and secondary carboxyl groups
D_K, effective dielectric constant within r
σ, statistical factor.

The statistical factor σ takes the value 4 for symmetrical dibasic acids, but $\sigma>4$ for unsymmetrical dibasic acids[8,9].

In Table 5, the pK_1° and pK_2° values and the differences, $\Delta pK'=pK_2^\circ-pK_1^\circ$, for the copolymers, (h) and (i), were compared with the values for low molecular weight compounds.

The pK_1° value for MA–VAc copolymer is a little lower than the pK_1 of α, β-diethyl succinic acids, (f) and (g). On the other hand, $\Delta pK'$ for MA–VAc copolymer is an intermediate value between dimethyl (e) and diethyl succinic acid (f).

The pK_1° value for MA–S copolymer is about 0.5 lower than the pK_1 of α-benzyl, β-ethyl succinic acid (s). On the other hand, $\Delta pK'$ for MA–S copolymer, 4.6, is very large compared with the values of α, β-dialkyl succinic acids.

Discussion

From the comparisons with the corresponding monomeric runs in Table 5, the following considerations are deduced, neglecting the disagreement of the temperatures measured.

1 pK_1° The variation of pK_1 values with substituents in monomeric runs indicates that the introduction of phenyl and benzyl group in place of methyl and ethyl results in a somewhat lower pK_1 value. The results in pK_1° for MA–VAc copolymer and MA–S copolymer can be explained from the above tendency, but the latter value is too low to be compared with the proper monomeric runs.

The contribution of the inductive effect of acetoxy ester group to the pK_1° value is considered to be small by comparing (a) with (c) in Table 5, even if the inductive effect of acetoxy ester group is the same as that of the ordinary ester group.

The influence of hydrogen bonding[10] on the pK_1 values will be considered in the next paragraph in relation to $\Delta pK'$ values.

2 $\Delta pK'$ The distance r and effective dielectric constant D_K calculated from the $\Delta pK'$ values by the use of Kirkwood-Westheimer theory[7] are given[11] in Table 6, for (a), (d), (e), (f) and (g) compounds in Table 5.

According to the Kirkwood model, the change of $\Delta pK'$ in Table 6 may be attributed mainly to the change of D_K, if the nonelectrostatic forces can be neglected.

However, another consideration must be taken into account when the nonelectrostatic forces

8) D. H. R. Barton and G. A. Schmeidler, *J. Chem. Soc.*, 1197 (1948)
9) H. Le Moal, *Bull. Soc. Chim. France*, 418 (1956)
10) C. Tanford, *J. Am. Chem. Soc.*, 79, 5348 (1957)
11) F. H. Westheimer and M. W. Shookhoff, *ibid.*, 61, 555 (1939)

Table 6 Calculated values of r and D_K

	(a)	(d)	(e)	(f)	(g)
$\Delta pK'$	1.29	2.21	2.26	2.83	3.09
r(Å)	5.75	5.35	5.30	5.10	5.00
D_K	50	29	28	21	20

such as hydrogen bonding[12,13] is concerned.

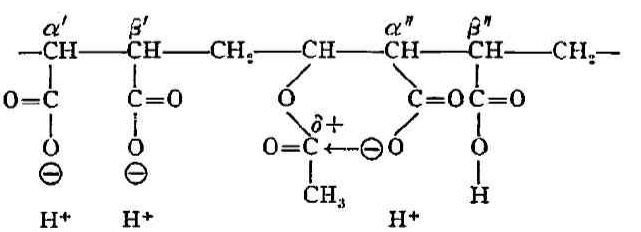
A simple evidence for the presence of hydrogen bonding is given by comparing the K_1 values for dibasic acids with the K_K values of the corresponding monomethyl ester[14]; that is, we can use the following statistical relation[8,9]:

$$K_1 = 2K_0 \quad \text{or} \quad K_1 = K_0^{\alpha} + K_0^{\beta}, \tag{7}$$

where K_1 represents the experimental first dissociation constant, and K_0, K_0^{α} and K_0^{β} represent the partial dissociation constants. Barton and Schmeidler[8] proposed to use the dissociation constants, K_K, K_K^{α} and K_K^{β} of the monomethyl esters in place of K_0, K_0^{α} and K_0^{β}. The calculated value of $K_1/2K_K$ or $K_1/(K_K^{\alpha}+K_K^{\beta})$ based on the dissociation constants of monomethyl ester[13,15] of (a), (d), (e) and (j) compounds in Table 5 are: (a) 1.0, (d) 1.4, (e) 1.3, (j) 1.03. These values are very small compared with maleic acid[12,13] (5.3), tetramethyl succinic acid[13] (13.5) and diethyl malonic acid[14,15] (16). Thus, although the hydrogen bonding presents itself, the contributions may be considered to be negligible.

It may be obviously considered that the presence of hydrogen bonding decreases the pK_1 values and increases the $\Delta pK'$ values[9]. If the pK_1° for MA–VAc copolymer exhibits lower value, owing to the hydrogen bonding between the primary carboxylate anion and the secondary carboxyl group, than the value for (f) or (g) compound in Table 5, the larger value of $\Delta pK'$ will be expected.

In that respect, Garrett's study[16] on the solvolysis of aspirin (in which an acetoxy ester group is located at the resemble place to an adjacent carboxyl group as in the MA–VAc copolymer) may be very suggestive. Garrett attributed the abnormal higher rate of hydrolysis of aspirin in neutral medium to the intramolecular ring formation[17] caused by the attack of o-carboxylate anion to the



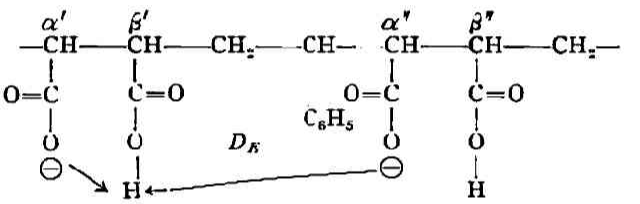
(A)

12) D. H. McDaniel and H. C. Brown, *Science*, 118, 370 (1953)
13) H. C. Brown, D. H. McDaniel and O. Hafliger, *Determination of Organic Structures by Physical Methods*, in Braude and Nachod, Academic Press Inc., New York, N. Y. (1955) p. 628
14) F. H. Westheimer and O. T. Benfey, *J. Am. Chem. Soc.*, 78, 5309 (1956)
15) *Landolt-Börnstein Tab.*, Hauptwerk
16) E. R. Garrett, *J. Am. Chem. Soc.*, 79, 3401 (1957)
17) J. D. Chanley, *ibid.*, 74, 4347 (1952)

carbonyl carbon in the ester.

As the carboxylate anion is obviously more nucleophilic than the carboxyl radical, the following neighbor interactions stabilize the dissociation of first class and make easy the dissociation of second class.

The tendency that the pK_1^c value is lower and $\Delta pK'$ is smaller than the corresponding values of α, β-diethyl succinic acid, (f) or (g). may be considered as due to the above interaction. The deduction means that the screening effect of comonomer —CH_2—CH(O $COCH_3$)— on the electrostatic interaction between the α''-carboxylate anion and the β'-carboxylate anion may be more effective (Fig. A). Thus, the pK_1^c and $\Delta pK'$ for MA-VAc copolymer may be regarded as rather reasonable values. On the other hand, the $\Delta pK'$ for MA-S copolymer is too large compared with the other α, β-dialkyl succinic acids. The above considerations lead to the following nearest neighbor interaction for the purpose of an interpretation for the larger $\Delta pK'$ value.



(B)

The work to dissociate the β'-carboxyl group must be done against the electrostatic repulsion forces due to the α''-carboxylate anion as well as the α'-carboxylate anion. The reduction of the screening effect of comonomer, —CH_2—CH(C_6H_5)—, to the repulsive force due to the α''-carboxylate charge means the decrease of effective dielectric constant D_K in the comonomer cavity (Fig. B). The obvious reason is the hydrophobic property of phenyl alkyl group.

Acknowledgements

The author is greatly indebted to Professor Ichiro Sakurada and Professor Wasaburo Jono of Kyoto University and to Professor Masamori Yamada of this University for their valuable guidance and kind encouragement. Thanks are tendered also to Professor Akio Nakajima of Kyoto University for his helpful discussion and critical reading of manuscript, and to the Ministry of Education for a grant-in-aid.

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